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Shock Induced Chemistry: Application and Development of Ultrafast
Nonlinear Probes of the Energy Dynamics of Molecules in Solids

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Under the contract (N00014-85-K-0409) we have made significant progress in a number of areas which have led to increased understanding of the dynamics of molecules in solids and in the development of new experimental techniques and associated theory for the investigation of solids and gas phase systems. This work will be briefly summarized in this section. A list of publications which have resulted from the research supported by this contract is given following the report.

A. Nonlinear Probes of the Interaction of Bulk Mechanical Degrees of Freedom with Molecular Electronic States

A molecule in a condensed matter system at finite temperatures experiences a wide variety of dynamical interactions with its environment. In general, the mechanical degrees of freedom of the host crystal will couple to the electronic states of the molecule of interest [1]. The time dependent fluctuations of this heat bath (host medium) strongly influence or dominate processes such as chemical reactions, electron transport, or energy transport. In addition to random heat bath fluctuations, other time dependent mechanical perturbations, e.g., coherently excited single phonon modes or shock waves, can interact

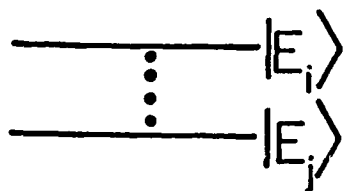
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strongly with impurities and defects in a crystal lattice or other medium [2,3].

In spite of the importance of the coupling between impurity electronic states and bulk mechanical states of the host medium, there are few experiments which are able to address the coupling directly [4,5,6]. We have developed a new approach to probing the coupling between bulk mechanical degrees of freedom and the internal electronic states of an impurity or other defect [7,8]. The observable in the first experiments to be described [7] is the time resolved coherent anti-Stokes emission arising from the bulk mode of interest in a low concentration mixed molecular crystal. The most striking feature of the data is its dependence upon the scenario chosen to coherently populate and probe the host phonon mode. If all wave lengths used in the CARS experiment are tuned well to the red of the impurity singlet state electronic absorption, and the pump and Stokes beams are adjusted such that $\omega_p - \omega_s$ is on resonance with the phonon, the decay of the anti-Stokes emission is identical to that of the same mode in the pure crystal. However, very different results are obtained when ω_p is tuned into the S_0 to S_1 electronic transition of the impurity molecule and $\omega_p - \omega_s$ is kept on resonance with the host crystal phonon. Figure 1 shows the off resonance (a) and on resonance (b) pumping schemes. Two dramatic changes take place. First there is a substantial resonant enhancement of the anti-Stokes emission from the bulk mode. Second, there is a threefold reduction in the decay time of the CARS signal from the bulk phonon. Figure 2 displays data taken on the naphthalene 69 cm^{-1} optical phonon in a pure crystal and in a mixed crystal. The mixed crystal data was taken with resonance enhancement by the pentacene



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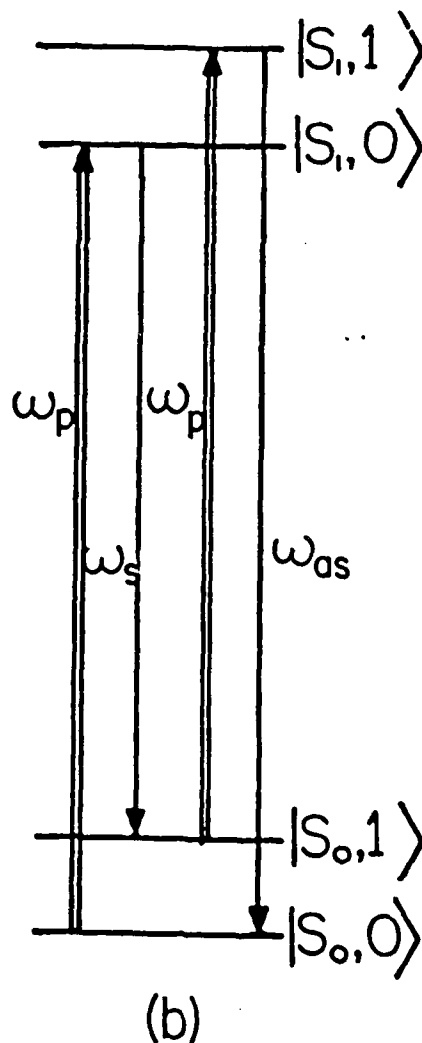
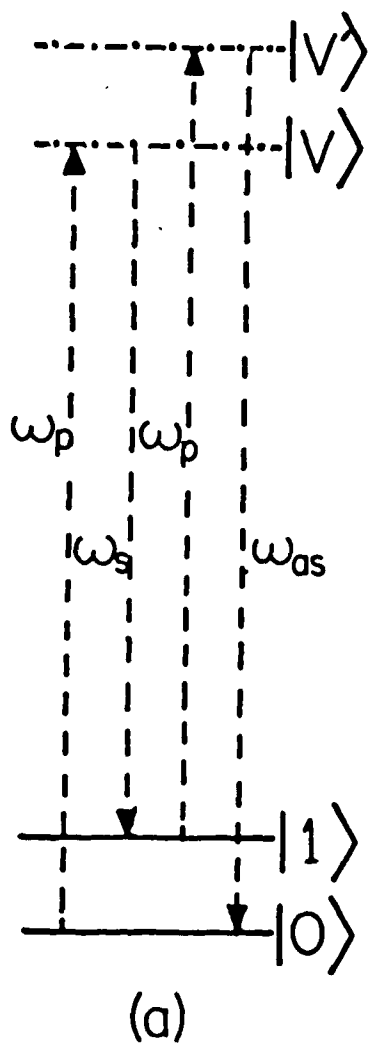


Figure 1

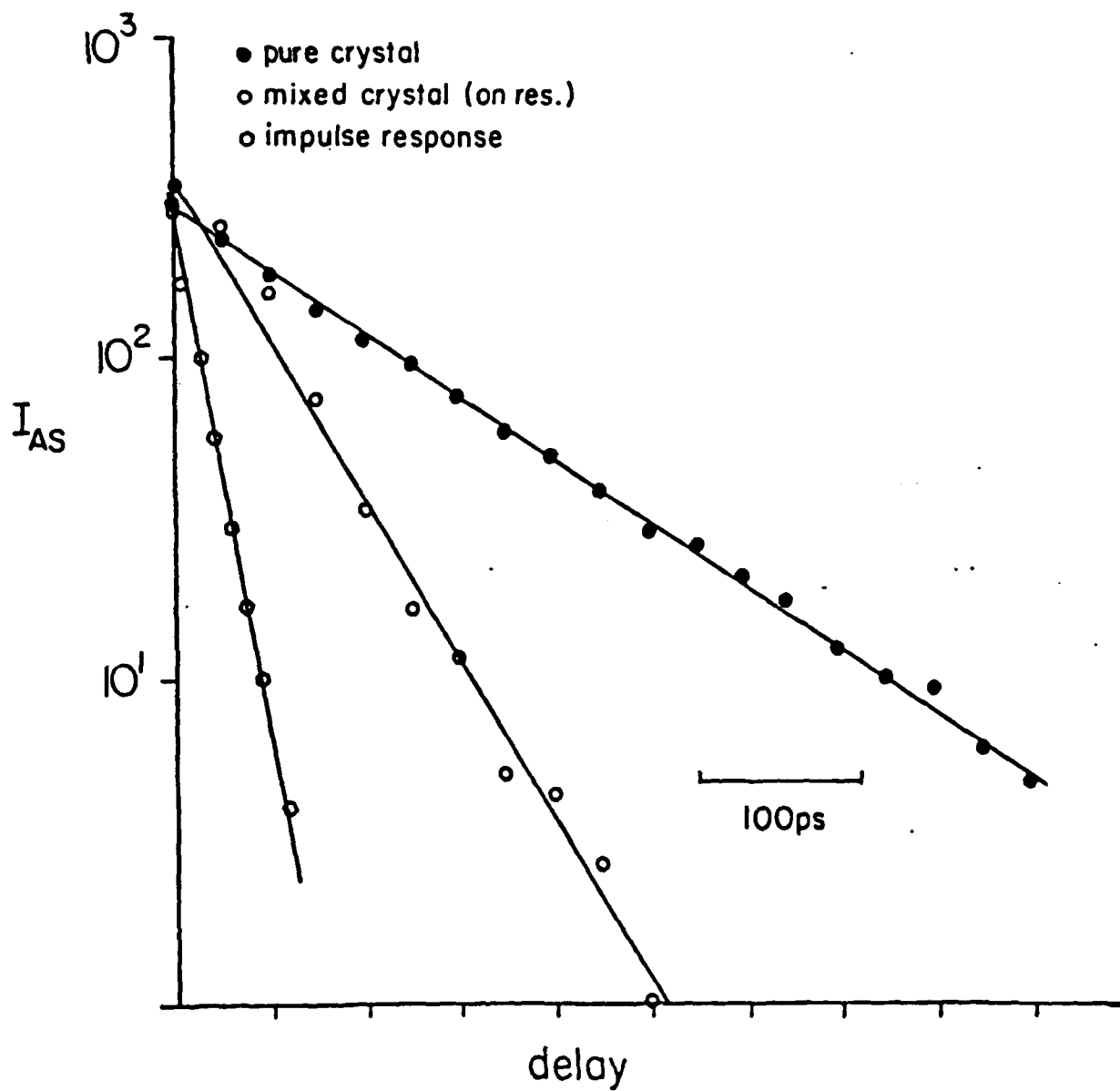


Figure 2

impurity. In the mixed crystal, data taken off resonance looks identical to the pure crystal data. The figure also shows the instrument response function.

The details of these observations as well as their implications about the nature of the coupling of a localized defect to the bulk modes of the crystal have been analyzed [7]. The resonant enhancement provides a direct probe of the coupling of the defect or impurity electronic states to the bulk mode propagating in the direction determined by the wave vectors of the excitation beams. Thus it is possible to probe the selective interaction of impurity electronic states with a particular bulk phonon, and it should be possible to obtain the directional anisotropy of the coupling. Observations pertaining to the change in the CARS decay on resonance demonstrate the existence of impurity perturbed domains, i.e., regions of the crystal associated with the impurity which are distinct from the bulk material.

In the impurity enhanced phonon CARS experiment, the impurity electronic state-phonon coupling resonantly enhances the production and detection of an optical phonon when the excitation wavelength is on resonance with the impurity electronic transition. The extent of the resonant enhancement is a measure of the phonon-impurity excitation coupling. Unlike the acoustic phonon sideband seen in absorption spectra, which has contributions from all phonon branches and phonons propagating in all directions, the impurity enhanced optical phonon CARS signal examines a single phonon propagating in a well defined direction. By changing the phonon propagation direction it should be possible to explore the directional anisotropy of the excitation-phonon coupling.

Tuning into various phonon modes and various electronic states will permit a range of phonon-electronic state interactions to be measured.

It was observed that the CARS decay, when enhanced by the impurity electronic transition, was significantly faster than the nonenhanced decay in the same crystal (see fig. 2). A variety of observations on the concentration dependence and the detuning dependence of the CARS decays strongly suggests the existence of impurity perturbed domains. The impurity perturbed domains have distinct mechanical characteristics which, to some extent, decouple them from the bulk crystal. This gives rise to two decay times, one associated with the bulk phonon in the mixed crystal and one associated with the phonon in the impurity perturbed domains. The bulk phonon decay in the mixed crystal is indistinguishable from the pure crystal decay, while the impurity perturbed domain phonon decay is considerably faster. These domains may be impurity induced defect regions of the crystal which are substantially larger than the single impurity molecule.

These experiments provide a new approach to the examination of the interactions of the internal electronic degrees of freedom of a molecule with the mechanical degrees of freedom of its environment. Since these interactions are fundamental to understanding dynamics and dynamical intermolecular interactions in solids, impurity resonant enhancement of bulk mode CARS experiments can add to our understanding of condensed matter systems.

We have also developed a detailed theoretical treatment of another new approach for the direct examination of the interaction of bulk mechanical degrees of freedom of a crystal with molecular electronic states [8]. We call the proposed new experiment the Phonon Perturbed

Photon Echo (P^3E). The approach circumvents the nonselective thermal excitation of phonons and excites a particular phonon by a stimulated Raman process at low temperature where the thermal population of phonons is negligible. The effect of the selective phonon excitation is then monitored with a photon echo pulse sequence. The phonon excitation is produced by two short time coincident laser pulses of different frequencies crossed in the sample. The phonon of interest is excited by tuning the difference of the laser frequencies to the phonon frequency and obeying symmetry selection rules and wave vector matching conditions. The phonon excited in this way is a coherent wave with well-defined phase and in this sense contrasts with thermally excited phonons. Shortly after this phonon excitation step the system is probed by a regular photon echo sequence.

The P^3E experiment closely parallels a magnetic resonance experiment in which the external field is modulated. In the optical experiment (in the limit of high phonon occupation), the phonon wave modulates the optical transition frequency of the impurity by electron-phonon coupling, producing frequency sidebands on the homogeneous absorption line, analogous to the NMR result. However, unlike the NMR case, the size of the sample in the optical experiment is large compared to the phonon wavelength, and therefore it is necessary to average over all phases of the modulation.

The influence of the phonon on the photon echo is distinctly different from the normal homogeneous dephasing measured in a conventional photon echo experiment. In a conventional echo experiment, random fluctuations in molecular site energies produced by thermally excited phonons, which span a wide range of frequencies and are

generated with random phases, destroy the phase relationships among the electronic coherent superposition states. The decay of the echo signal as the time between the two echo excitation pulses is increased, measures the time dependent decay of the electronic excited state phase. The echo measures the decay of the off diagonal matrix elements of the reduced density matrix which describes the electronic states. The echo decay is the Fourier transform of the homogeneous electronic absorption line.

In the P^3E experiment, a single phonon wave with well defined wave vector, frequency and phase is generated. This does not cause homogeneous dephasing, i.e., it does not result in an irreversible loss of the phase relationships among the electronic superposition states. Rather, electron-phonon coupling causes the transition frequency of each isochromat to oscillate instead of randomly fluctuate. This causes a reduction in the magnitude of the echo signal. In the absence of phonon damping, this reduction is independent of the pulse separation in the echo pulse sequence. This effect is not conventional phonon induced dephasing.

The change in the echo signal pulse area is directly related to the amplitude of the phonon wave and the excitation-phonon coupling matrix element. Since the phonon amplitude can be determined by CARS or other methods, the electron-phonon matrix element can be determined. By generating the phonon with various propagation directions, directional anisotropy in the matrix elements can be mapped out. The coupling of electronic states to different phonon modes can also be investigated because of the selective excitation of the phonon.

B. Dynamics of Electronic State Energies on Fast and Slow Time Scales

One of our most important accomplishments of this contract period has been a series of experiments and theoretical developments which are revolutionizing the way optical experiments are used and interpreted in the investigation of solids with time evolving structures [9,10,11,12,13,14,15]. In glasses, complex crystals, proteins and other condensed matter systems, in addition to phonon induced fluctuations of local mechanical properties, there can be much slower timescale structural evolution.

The local structures associated with a glassy system are not static even at very low temperatures (1.5 K) [16]. In organic glasses, small potential barriers separate different local mechanical configurations. Tunnelling and thermal activation result in constantly changing solvent structures. This is in contrast to a simple crystal in which phonon induced fluctuation occur about a single equilibrium lattice structure.

Anderson and co-workers [17] and Phillips [18] independently proposed a model based on the Two-Level System (TLS) to describes structural dynamics in glasses. TLS represent extra degrees of freedom characteristic of the glassy state. Briefly, a TLS is composed of two distinct local potential minima separated by a barrier. Changes in local glass structure are modeled as transitions between the two potential minima. There are a wide distribution of energy differences of the TLS potential minima and a wide distribution of tunneling

parameters which are responsible for transitions between local configurations. Thus there is a very wide range of time scales associated with the dynamics of the TLS.

In addition to direct phonon induced fluctuations, the changes in the local configuration of a glass or crystal can modulate the electronic state energies of a molecule. If the molecules were not coupled to the environment, an absorption spectrum would reveal a line broadened only by the electronic excited state lifetime (T_1). Since the chromophore is coupled to environment the energy levels fluctuate yielding a broader linewidth (frequency domain description) or alternatively a shorter dephasing time (time domain description). An absorption spectrum of a chromophore in a glass or a crystal will also be inhomogeneously broadened. Inhomogeneous broadening is a result of the wide variety of static local environments. To extract dynamical information from the dephasing of electronically excited chromophores, it is necessary to obtain lineshape information with inhomogeneous broadening removed.

The electronic state energies of chromophores in a glass will be affected by processes in the medium which occur on a wide variety of time scales. The time scales will range from extremely fast fluctuations, to much slower configurational changes, and finally totally static inhomogeneities. Because of the variety of time scales on which the medium affects the chromophore transition energies and therefore optical dephasing, it is necessary to carefully consider the sensitivity of various spectroscopic observables to the distribution of time scales.

Dephasing experiments have traditionally been treated with optical absorption formalisms. That is, the lineshape is related to the Fourier transform of a two-time dipole-moment correlation function. The optical absorption experiment is the Fourier transform of the optical free induction decay. It is sensitive to all time scales from the fastest fluctuations to the static inhomogeneities. In a glass system, the inhomogeneous broadening will mask the dynamical information of interest. The two time correlation function is not an appropriate description for line narrowing experiments such as photon echoes or hole burning experiments which are actually performed in chromophore-glass systems [15]. We have recently developed an appropriate formulation for the interpretation of line narrowing experiments used to study complex systems. We have been able to derive the correct four time correlation functions which properly describe the line narrowing experiments [15].

The photon echo experiment [19] is a special case of line narrowing experiment describable by the four time correlation function. In the echo experiment, a pulse of light resonant with the optical transition of the chromophore excites the sample at time $t = 0$. A second pulse excites the sample at $t = \tau$. The echo, a coherent pulse of light, emerges from the sample at $t = 2\tau$. The intensity of the echo is measured as a function of the pulse separation, τ . The echo pulse sequence removes static inhomogeneity from the optical dephasing measurement. It measures optical dephasing induced by random fluctuations on the timescale of τ .

Previously, all optical line narrowing experiments have been described in terms of the two time dipole correlation function. We have proven that the correlation function which describes hole burning

experiments, fluorescence line narrowing experiments, accumulated grating echo and incoherent photon echo experiments, and other line narrowing experiments, is the same as that which describes the stimulated photon echo [15]. In fact the hole burning experiment and the other experiments are the Fourier transform of the stimulated echo experiment. The stimulated echo is a three pulse sequence developed in magnetic resonance to measure spectral diffusion. There are two time scales in all of the optical line narrowing experiments except the photon echo. The first is τ , as in the echo experiment. The second is a much longer time, T_w . Optical experiments describable in terms of the stimulated echo four time correlation function will eliminate static inhomogeneous broadening, but will be sensitive to slow dynamics on the timescales out to the time T_w . For fluorescence line narrowing, T_w is on the order of the fluorescence lifetime. For phosphorescence line narrowing and accumulated grating echoes, T_w is on the order of the triplet state lifetime. In a whole burning experiment, T_w is on the time scale required to perform the experiment, i.e. write and read the hole. In a typical experiment, this is approximately 100 seconds. The photon echo experiment is the limit of all four time correlation function experiments in which T_w goes to zero. Therefore the echo experiment, in a system in which there exists a wide distribution of time scales of dynamics, will yield the narrowest spectroscopic line. It is sensitive to only the fastest dynamics on the timescale of τ .

The important point is that each of the four time correlation function experiments is sensitive to dynamics on a different timescale. Since complex systems exhibit a wide distribution of time scales for dynamics and therefore optical dephasing, a combination of the echo

experiment, which measures the homogeneous dephasing, and experiments such as hole burning, in which T_w is not zero, which measure homogeneous dephasing and slower spectral diffusion processes, can provide a detailed picture of the multitime scale dynamics.

We have obtained the first experimental comparison of line narrowing experiments which operate on different time scales by performing both picosecond photon echo experiments and nonphotochemical hole burning experiments on the same systems of molecules in organic glasses [10-15]. We have reported the results of temperature-dependent, hole burning and photon echo experiments on a dye molecule, resorufin, in ethanol, deuterio-ethanol, and glycerol glasses. The temperature was varied between 1.5K and 11K for the ethanol and deuterio-ethanol samples and between 1.1K and 25.5K for the glycerol samples. The echo decays and hole widths were found to be independent of wavelength. The echo experiments were tested for optical density effects, concentration effects, sample heating effects, power dependent effects. In all cases the echo results were consistent and free of artifacts. The hole burning experiments were carefully performed to avoid broadening of the holes by excessive power, burn time or hole depth. In the resorufin ethanol glass discussed below, holewidths agreed perfectly with those from another laboratory [14,20].

A typical hole (A) and echo decay (B) are shown in Fig. 3. All of the holes were Lorentzian and all of the echo decays were exponential. Note that the echo decay is single exponential over many factors of e . The temperature dependencies of the echo and hole burning experiments for resorufin in ethanol glass are shown in fig. 4. Figure 4 is a log-log plot of the temperature dependent hole burning dephasing times

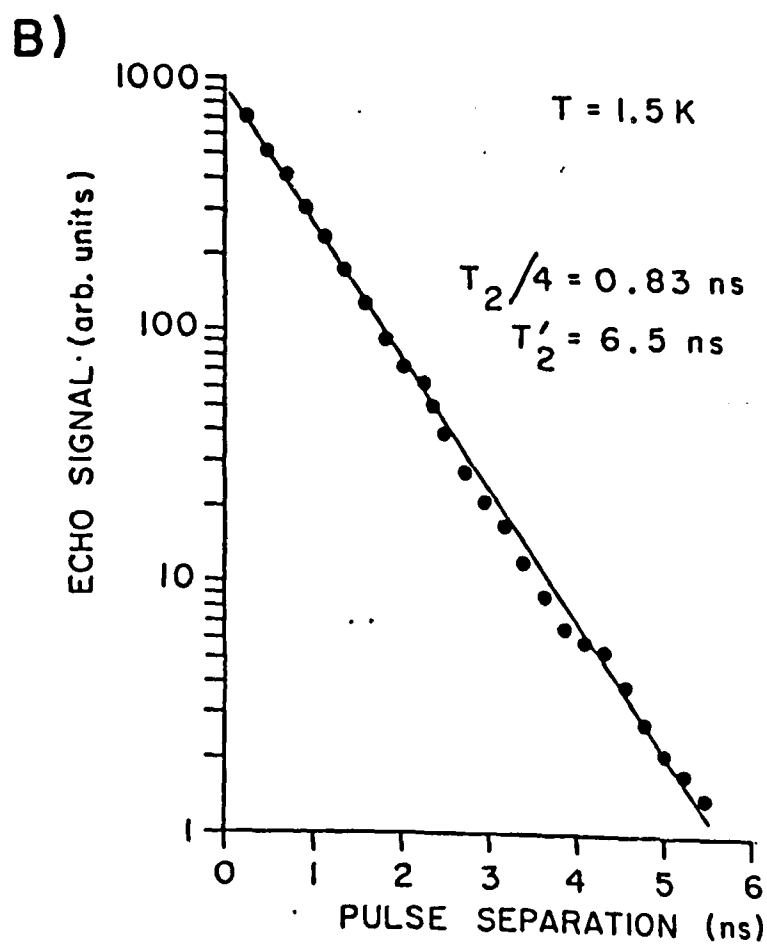
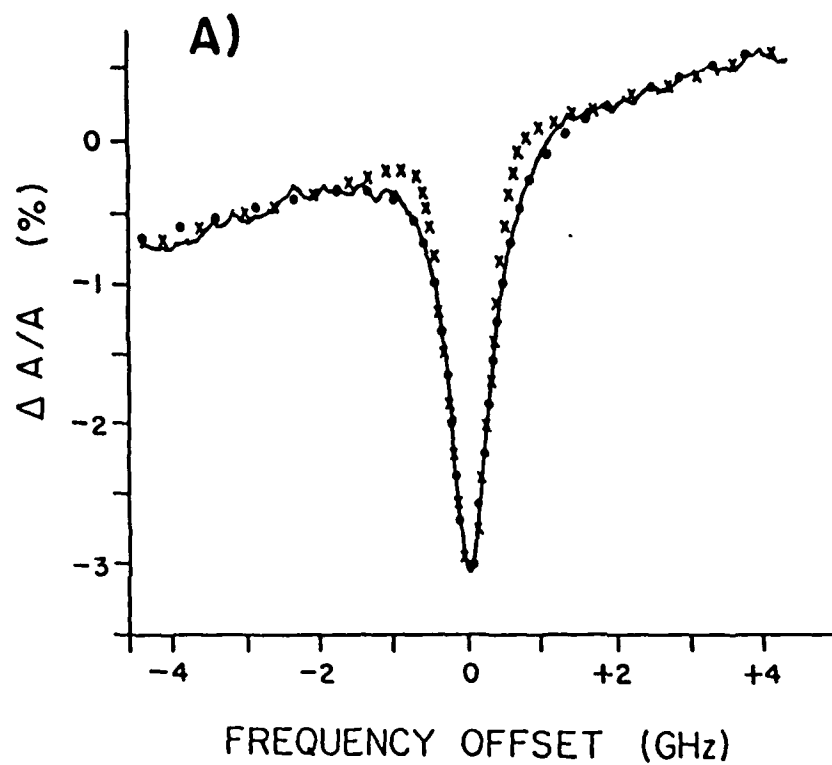


Figure 3

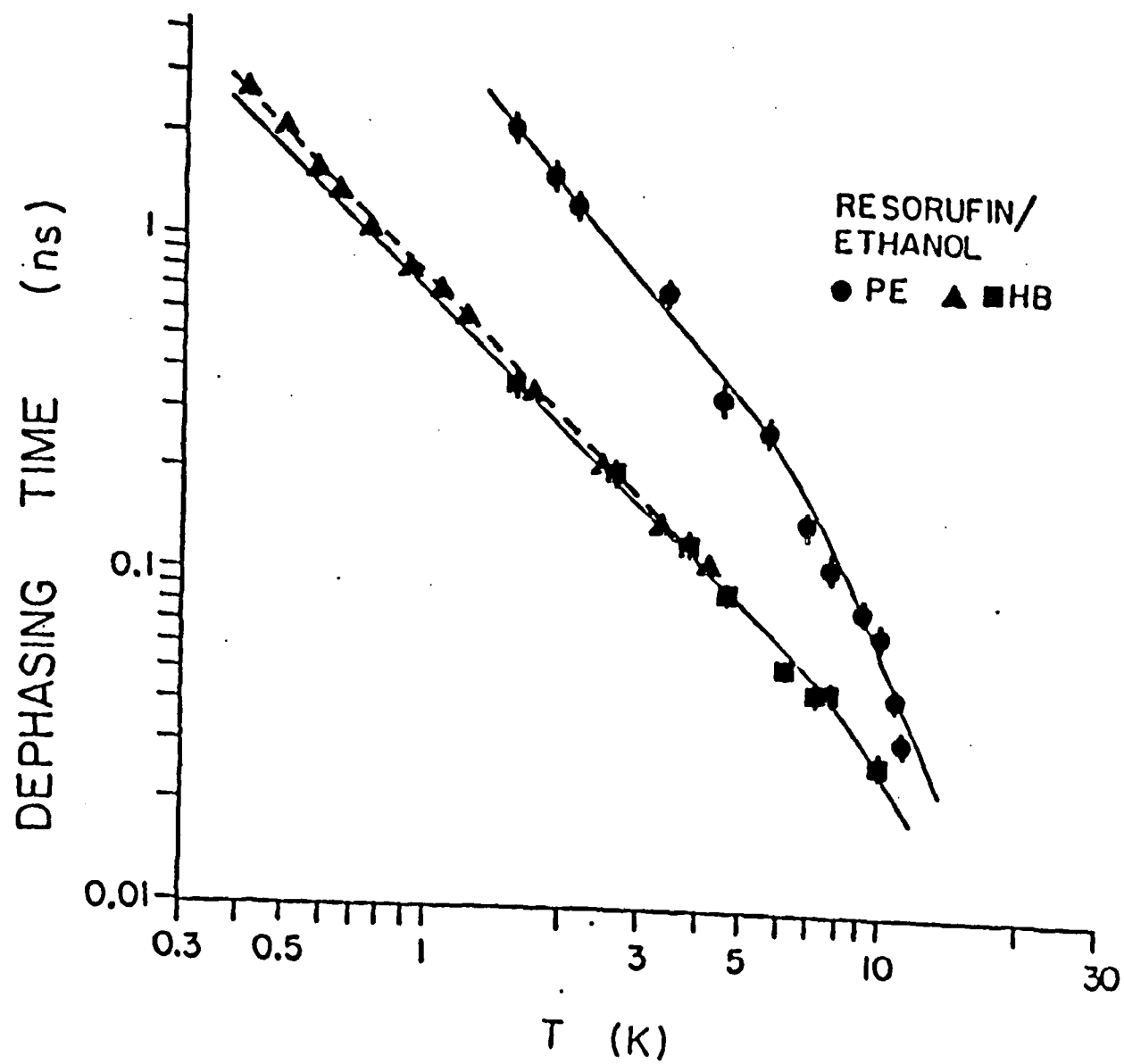


Figure 4

$[2/\pi(\text{FWHM})]$ (squares) compared to photon echo dephasing times (circles) for resorufin in ethanol glass. The hole burning data of van den Berg and Volker are also shown (triangles) [20]. The fluorescence lifetime contributions have been removed from all measurements. The hole burning and photon echo measurements give different results because spectral diffusion (slow time scale energy evolution) contributes significantly to the hole widths. The solid lines are the best fits of our data to equations developed based on our detailed analysis of the four time correlation function descriptions of the experiments. The dashed line results from slight adjustment of spectral diffusion parameters for the best agreement with the low temperature data of van den Berg and Volker.

The formal theoretical evaluation of the correlation functions briefly described above yields a simple procedure for combining echo and hole burning data to obtain a separation of information on fast and slow dynamical processes. The theoretical treatment shows that subtracting the homogeneous linewidth determined by the echo experiment from the linewidth determined from hole burning experiments on the same sample at the same temperature provides a direct measure of the spectral diffusion. We call this difference in widths Γ_{SD} , where the SD stands for spectral diffusion. The temperature dependencies of Γ_{SD} in glycerol and ethanol are shown in fig. 5. This is the first determination of the rate and temperature dependence of spectral diffusion in a glass.

Dephasing processes in complex systems occur over a wide range of timescales. The photon echo experiments were shown to measure the homogeneous dephasing time of the solute in the glass whereas the hole burning data includes additional contributions from long term spectral diffusion. The material discussed briefly above demonstrates that

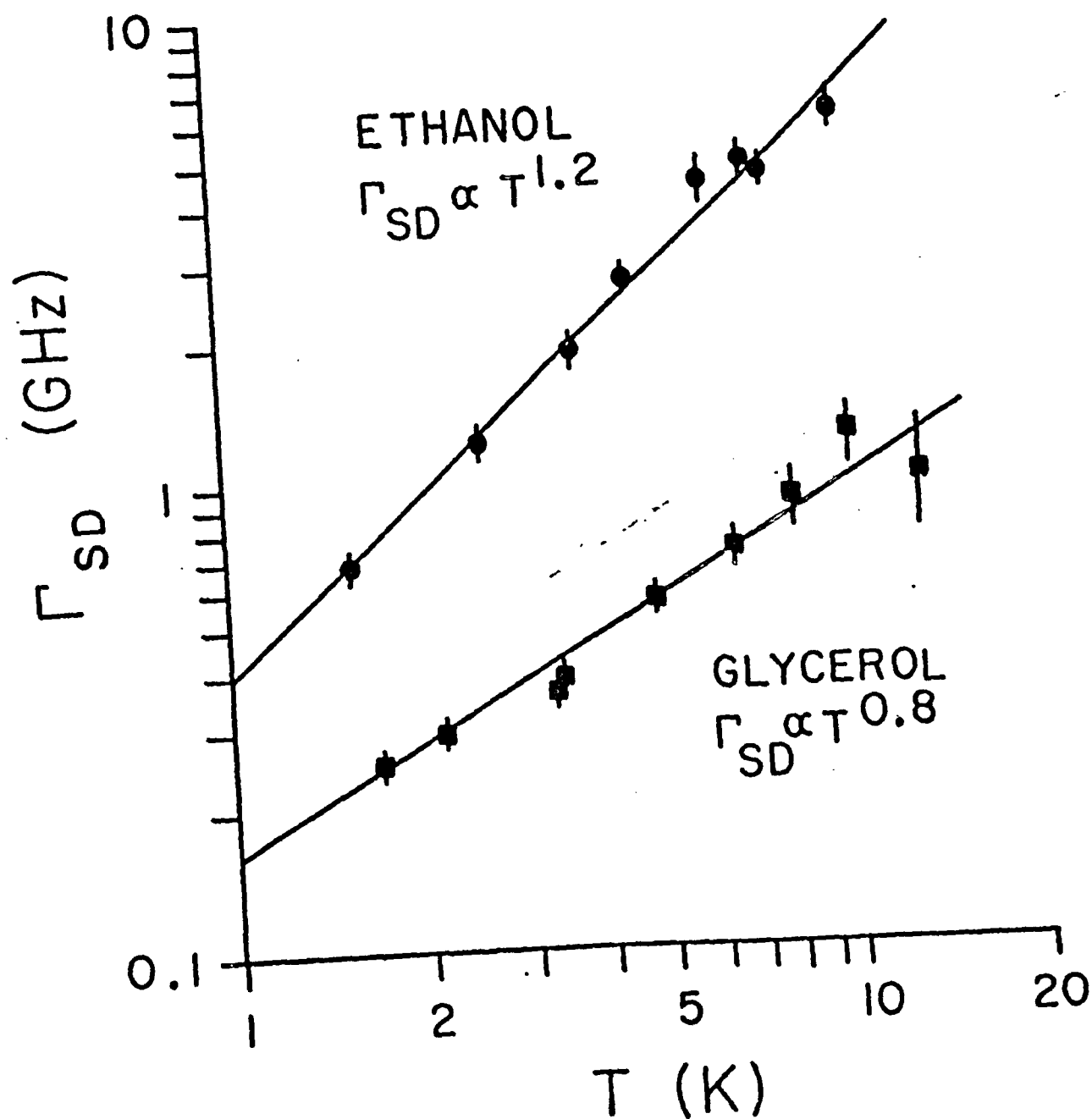


Figure 5

experiments on a variety of time scales can give a more complete picture of complex dynamics than any one technique can. All optical line narrowing experiments performed to date are describable in terms of appropriate four time correlation functions. Attempts to describe the experiments in terms of two time correlation functions mask the important distinctions among experiments. Combining echo experiments which provide a measure of the fast fluctuations with slower time scale experiments, such as hole burning, which are also sensitive to the slow dynamics of structural rearrangements, will provide detailed insights into the dynamics in complex systems.

C. Phase Related Picosecond Optical Pulses

Although in the past several years the application of optical coherence techniques to the investigation of the properties of systems of atoms and molecules has become increasingly sophisticated, optical techniques can not yet employ many of the methods common in magnetic resonance. Like magnetic resonance, optical pulse sequences have pulses with well defined durations, amplitudes, and time separations. However, in general the optical experiments do not make use of phase relationships among the pulses, although phase relationships are of fundamental importance in all but the simplest magnetic resonance techniques [21].

In the optical regime, photon echo and stimulated photon echo, and other phase independent techniques have been used to probe optical dephasing and population dynamics. Phase coherent pulse sequences in the microsecond and submicrosecond ranges, produced using acousto-optic

phase shifting techniques to modulate a CW laser, have been employed [22].

We are developing a new approach which produces phase related pulses on a 10 picosecond time scale [23]. The method is general and can be applied on a subpicosecond time scale as well. It involves actively stabilizing the phase relationship between picosecond pulses. A single tunable pulse is obtained by cavity dumping a dye laser synchronously pumped by the doubled output of an acousto-optically mode-locked and Q-switched Nd:YAG laser. A single pulse is beam split into two pulses, one of which transverses a optical delay line having a maximum delay of 9 nsec. In addition to the long delay, there is a piezo-electric translator (PZT) adjustable delay, which provides delays on an angstrom distance scale. This "phase scan PZT" permits the phase of one pulse relative to the other pulse to be scanned. The two pulses are recombined with a 50% beam splitter and directed into the sample cell. The sample cell is an evacuated optical cell containing sodium (Na) metal. The cell is heated to 500 K to produce a low pressure of Na vapor. The laser is tuned to one component of the Na D line. Fluorescence following excitation is detected at a right angle with a photo tube and a lock-in amplifier.

To stabilize the phase relationship between the two pulses, a small amount of each beam is picked off. The picked off pieces are combined with a beam splitter, and their path lengths are adjusted so the pulses are temporally coincident. The time and spatially coincident pulses form an optical interference pattern. This pattern is observed with a photo diode. After intensity normalization for shot-to-shot laser fluctuations, the signal produced by the interference pattern will

change with shifts in phase of the pulses. This signal is a phase error signal, and it is used in a feed back circuit to drive a second PZT delay in one of the main beams. This locks the phase relationship between the two pulses.

The phase scan PZT is down stream from the phase lock PZT. When the voltage to the phase scan PZT is ramped, the phase relationship between the two pulses is scanned. This can be detected as an oscillation in the intensity of the Na fluorescence as the phase is scanned. The pulses have been delayed in time so that they do not overlap in time. However, the delay is less than the Na free induction decay caused by the Doppler width of the transition. The first pulse generates a coherent superposition of the ground and excited electronic states. If the second pulse is brought in in-phase with the first, it will tip the vector which represents the coherent superposition further toward the excited state, and the fluorescence will be a maximum. If the second pulse is brought in 180° out of phase with the first, the vector will be tipped toward the ground state, and less fluorescence will occur. In the experiments we have swept the phase and observed well defined oscillations of the fluorescence. Figure 6 shows some typical data. This experiment conclusively demonstrates that the atomic system is experiencing optical pulses with well defined phase relationship. This phase dependent interaction is made possible by locking the phase relationship between the pair of picosecond pulses.

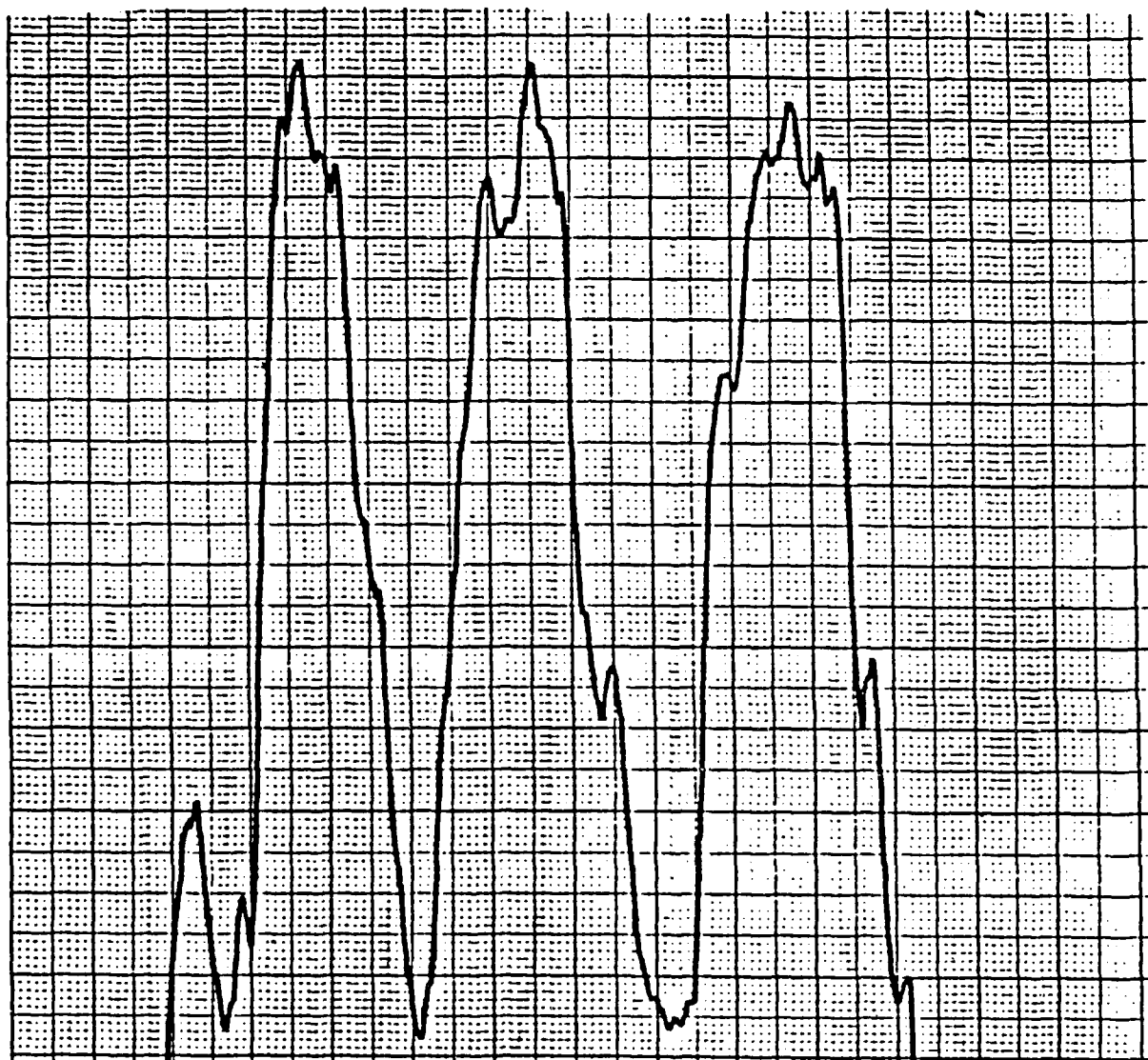


Figure 6

D. Gas Phase Dynamics and Spectroscopy Probed with Picosecond Transient Grating Experiments

Picosecond transient grating experiments [24] have been applied recently to the study of gas phase dynamics and spectroscopy for the first time in this laboratory [25,26,27]. The approach has tremendous potential for the investigation of gas phase problems, and may be particularly useful in the study of flames, combustion, and plasmas. Our work to date has elucidated three different aspects of the gas phase application of the picosecond transient grating experiment. First, theory and experiments on very low pressure Na vapor demonstrate that the time dependent transient grating signal can be used to measure the translational motion of atoms and molecules [26,27]. In fact the grating signal decay is related to the Fourier transform of the gas velocity distribution. Second, theory and experiments on moderate pressure I_2 vapor illustrate the effects of state changing collisions on the transient grating signal [27]. Analysis of the data leads to a determination of the collision cross section associated with the state change. It also provides data on the velocity distribution of the molecules following the state changing collision. Finally theory and experiments on Na vapor are used to elucidate a new type of time domain, ultrahigh resolution spectroscopy [26,27]. The experiments involve the time dependence of a polarization grating. Unlike the more conventional population grating methods, the polarization grating, when applied to Na, displays a time-dependent signal with pronounced oscillations at the Na ground state and excited state hyperfine frequencies. This is a Doppler free measurement.

The grating approach is inherently different than other methods used to study gas phase dynamics and spectroscopy. In addition to being sensitive to populations and spectroscopic properties of an atom or molecule, the picosecond transient grating experiment examines the spatial position of molecules as a function of time, and thereby obtains velocity information directly.

The grating works in the following manner. Two time coincident picosecond laser pulses of the same wavelength are crossed in the sample. Interference between the two coherently related pulses creates an optical fringe pattern in the sample such that the intensity of light varies sinusoidally in the beam overlap region. The spacing of the interference fringes is determined by the angle between the beams and by the wavelength of the light. When the frequency of the excitation pulses coincides with an absorption band of the gas phase molecule, excited states are produced. These excitations initially will have the same spatial distribution as the sinusoidal optical interference pattern, i. e., there will be an oscillatory spatial variation in the concentration of excited states. After a suitable time delay, a probe pulse (which may differ in wavelength from the excitation pulses) is directed into the sample along a third path. The probe pulse experiences an inhomogeneous optical medium resulting from the regions of high and low concentrations of excited states. These alternating regions have different indices of refraction, and consequently, a spatially periodic variation in the index of refraction is established. Thus, the probe pulse encounters a Bragg grating which causes it to diffract into one or more orders [24].

The excited molecules will move from regions of high excited state concentration, grating peaks, to areas of low excited state concentration, grating nulls. The translational motion will fill in the grating nulls and deplete the peaks. Destruction of the grating pattern by spatial redistribution of the excited molecules leads to a decrease in the intensity of the diffracted probe pulse as the probe delay time is increased. Thus, the time dependence of the grating signal is directly influenced by the translational motion.

In the Na experiments conducted to date, the gas is in thermal equilibrium. Therefore the velocity distribution is a Maxwell-Boltzmann distribution, i. e., a Gaussian. Figure 7 displays Na transient grating data. The signal decay is the product of an exponential lifetime decay and a Gaussian which is the Fourier transform of the Maxwell-Boltzmann distribution. (The spike in the data at time $t = 0$ is a coherence effect which decays at a rate determined by the free induction decay of the Doppler broadened line.) The solid line through the data is a theoretical fit with the temperature, T_f , as the only adjustable parameter. The temperature of the cell, T , was measured with a resistance thermometer on the body of the cell. The agreement is near perfect. This demonstrates that we have a detailed understanding of the experiment and that it is possible to make spatially resolved temperature measurements with the transient grating decay. The method can be extended to systems which are not in thermal equilibrium. For example, the velocity distributions of fragments from a photodissociation reaction can be examined.

In the experiments conducted on I_2 , the pressure is sufficiently high that there are collisions on the time scale of the transient

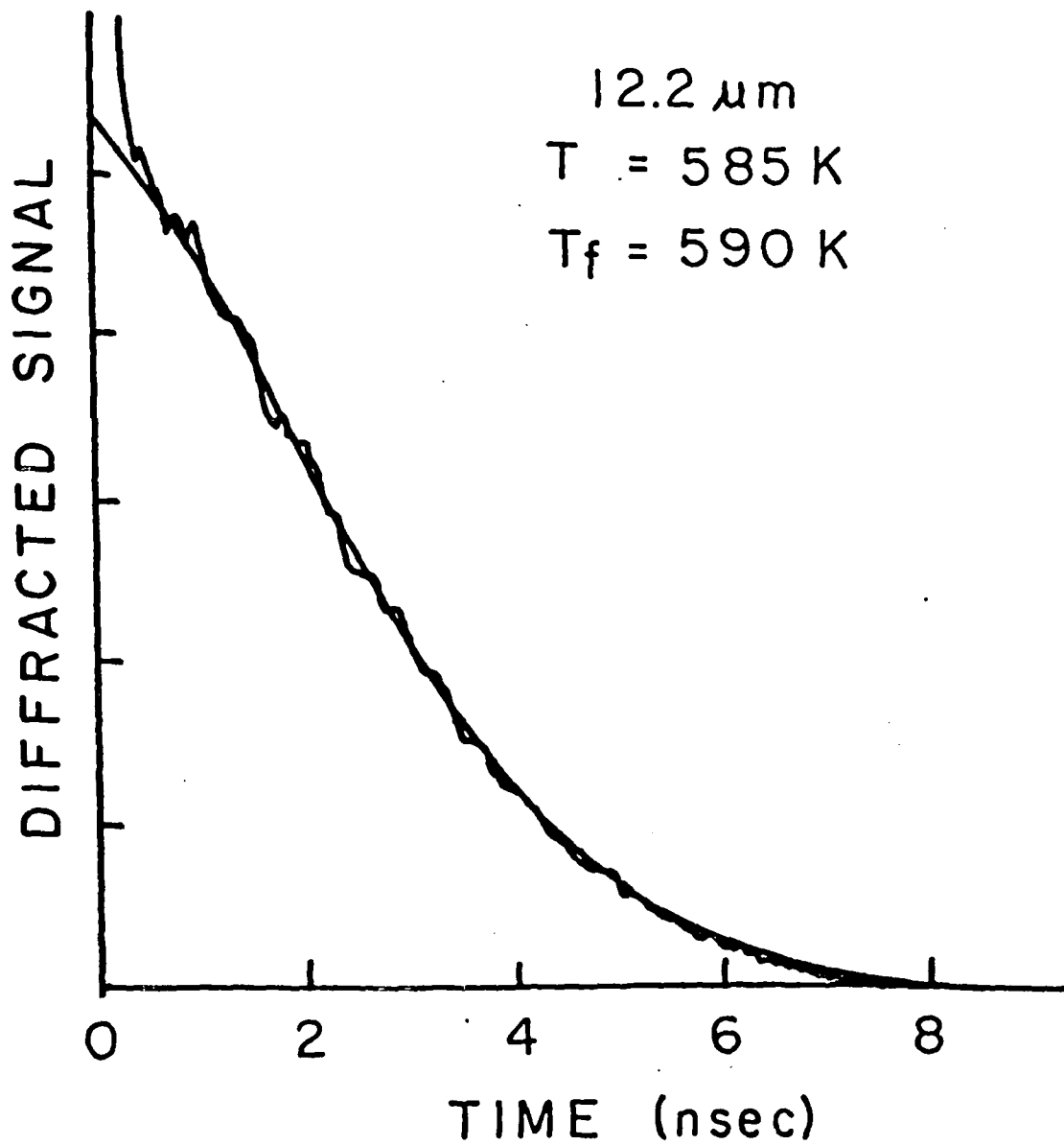


Figure 7

grating experiments. The state that is populated via collisions absorbs the probe strongly, and therefore, gives rise to a large diffraction efficiency. The time dependence of the transient grating signal is a competition between the growth of an observable grating caused by collisions and the destruction of the grating pattern resulting from the translational motion of the molecules. Figure 8 shows data taken at a variety of fringe spacings. As the fringe spacing becomes smaller, it takes less time for molecules to move from grating peaks to nulls. Therefore it takes less time for the grating to be destroyed by translational motion. The signal carries information on the initial velocity distribution, the collisional process, and the velocity distribution of those molecules which scatter into the observable state. The solid lines through the data are theoretical fits based on a model we have recently developed [27]. The detailed theoretical modeling shows that the collision cross section for the state change is somewhat smaller than hard sphere, and that the state changing collision randomizes the initial velocity. The temperature of the velocity distribution of molecules which have collided is very close to the initial temperature. These experiments are somewhat analogous to a molecular beam experiment, but the information is obtained by optically labeling molecules with the grating pattern.

The experiments examining translational and collisional phenomena on Na and I_2 employ population transient gratings. In another set of Na experiments, the excitation beams have perpendicular polarizations which gives rise to a polarization grating. Figure 9 displays data taken under identical conditions as in fig. 7, but the trace was taken with the polarization of one of the excitation beams rotated 90 degrees

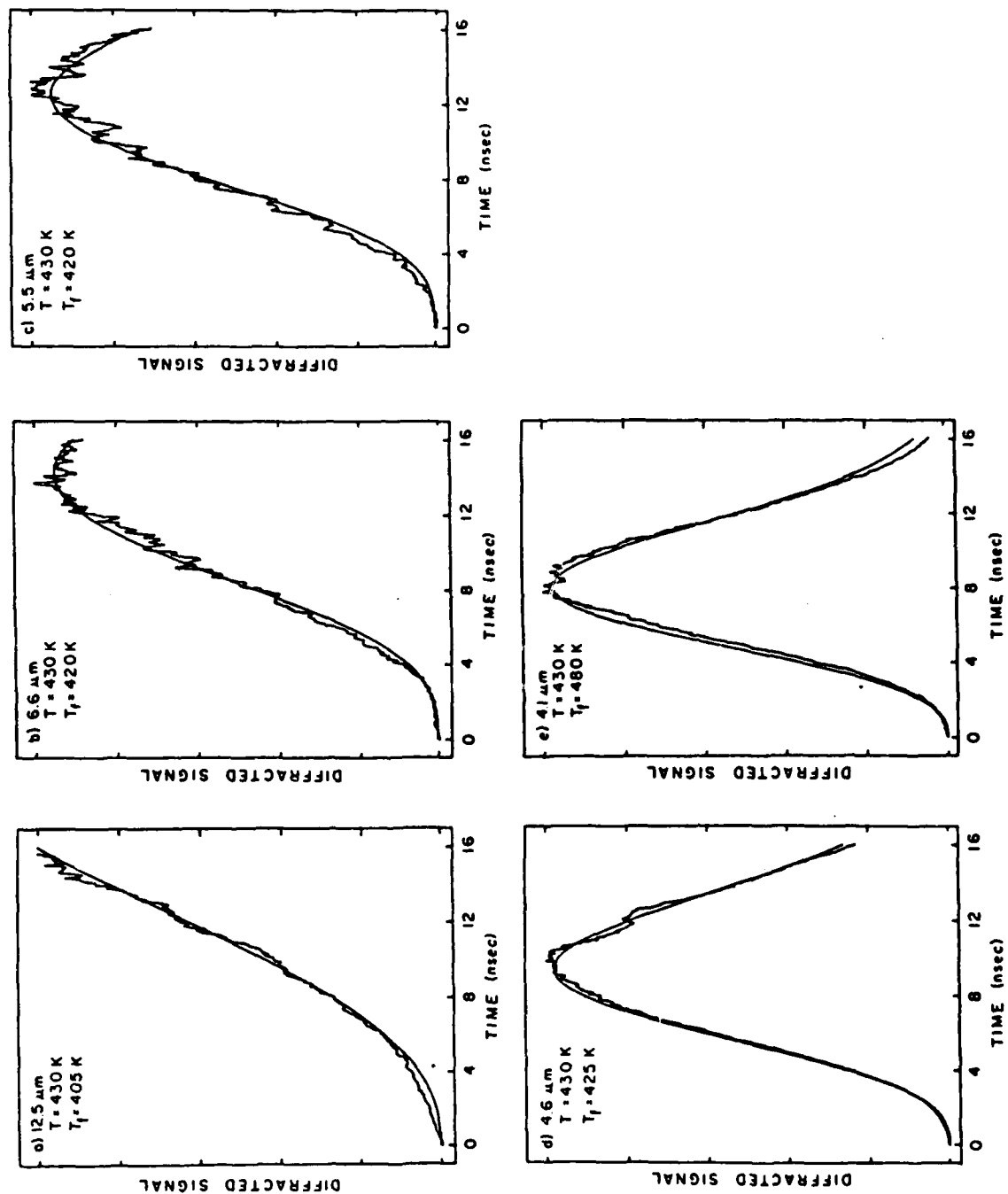


Figure 8

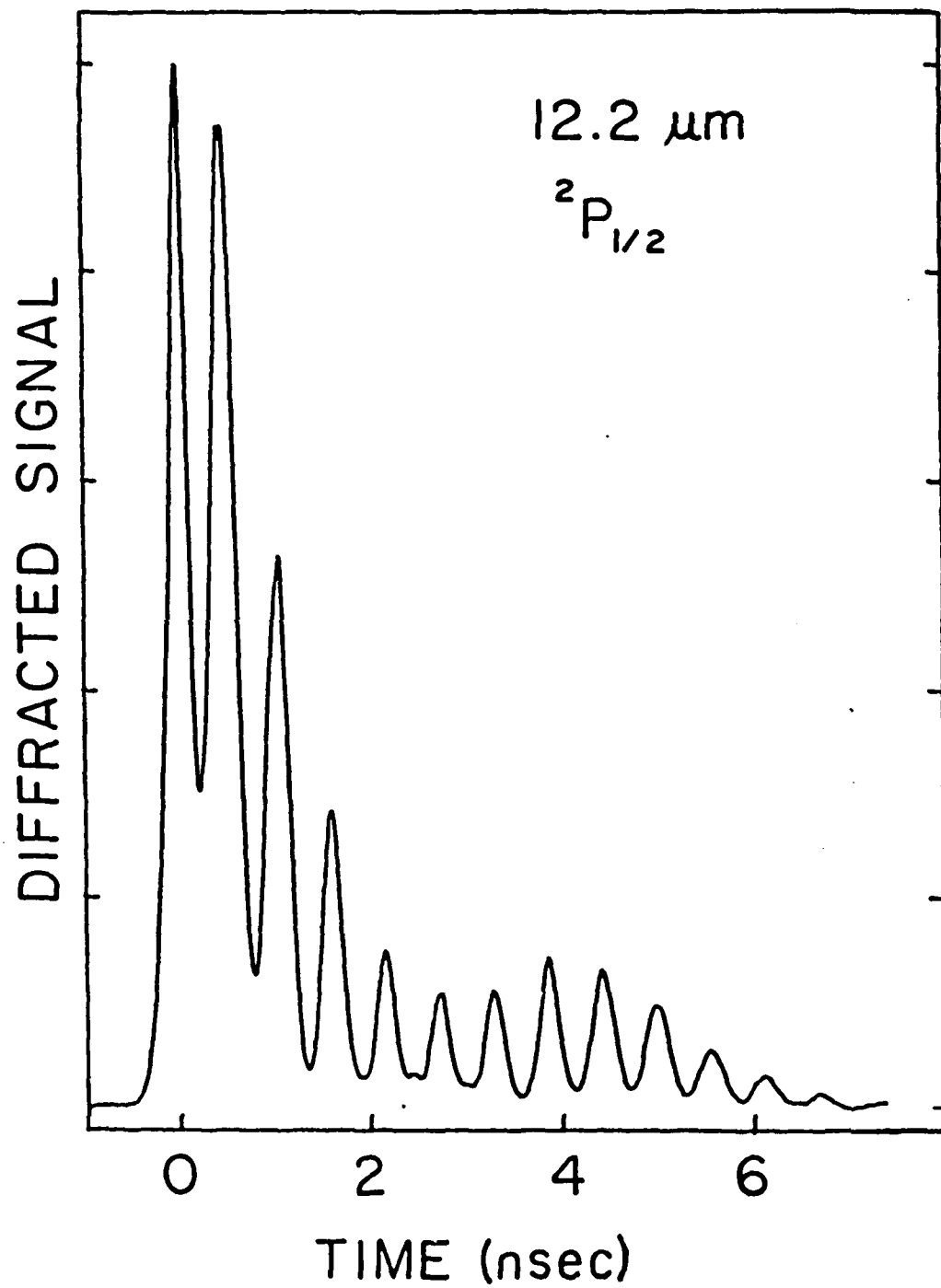


Figure 9

to form a polarization grating. The appearance of the oscillations in the data is quite dramatic.

The signals in the Na polarization grating experiments exhibit oscillations that are characteristic of the ground and excited state hyperfine frequencies (1.77 GHz and 189 MHz, respectively). The theoretical analysis [27] demonstrates that the observed oscillations in the grating signal stem from the spatial anisotropy of the excitation conditions. The detailed theory shows that the oscillations should vanish for a population grating (parallel excitation polarizations).

The unique time behavior of the Na polarization grating is expected to occur whenever there exist manifolds of states with selection rules for the change in the M angular momentum quantum number of $+1$ and -1 . Gas phase molecules have rotational states with well defined M values and $+1$ and -1 selection rules. Therefore, polarization grating spectroscopy should be useful in the study of rotational state spectroscopy and dynamics.

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